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(54) Title: MOLECULAR-ELECTRONIC DEVICES

(57) Abstract

Derivatives of macrocyclic compounds capable of forming columnar stacks in the solid phase such as porphyrin and phthalocyanines which are capable of forming hydrogen bonds have been found to exhibit enhanced conduction properties. A preferred compound is mesotetrakis(2-imidazolyl)porphyrin. The derivatives may exhibit proton conductance. The 1:1 metal complexes are valuable in so far as they may exhibit both protonic and electronic conduction.

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MOLECULAR-ELECTRONIC DEVICES

This invention relates to novel molecular-electronic devices which comprise conducting species; to processes for the
5 production of the conducting species and to certain novel conducting compounds.

One class of compounds which have been proposed as having potentially valuable conduction properties are macrocyclic compounds which are capable of forming columnar stacks in the
10 solid state. Examples of such compounds include phthalocyanines and porphyrins. The formation of metal complexes of such compounds or the introduction of suitable dopants has been found to enhance the conduction properties of these compounds. These prior proposals have all been directed to compounds wherein the
15 mode of conduction is electronic.

We have now discovered that derivatives of macrocyclic compounds which comprise substituents which are capable of interacting to form a hydrogen bond may exhibit proton conductivity. Furthermore, the bond formation facilitates the
20 formation of ordered molecular stacks and this enhances the ability to form useful conducting materials.

Accordingly, from one aspect this invention provides a molecular-electronic device wherein the conducting material comprises a macrocyclic compound which is capable of forming
25 columnar stacks wherein said compound comprising at least one substituent capable of forming a hydrogen bond as part of its molecular structure. In a preferred embodiment the conducting material is such that the mode of conduction is at least partially that of proton conduction.

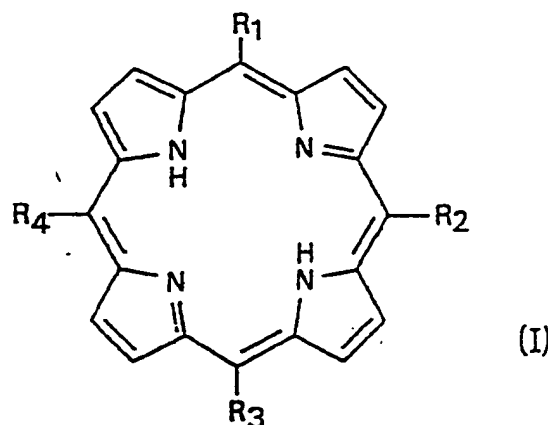
The derivatives which we have found to be useful are those which contain substituents which facilitate the formation of hydrogen bonds between the molecular layers in the columnar stack. The nature of the substituent groups which are capable of forming such bonds is well known in the art. The preferred
35 derivatives for use according to this invention are those in

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which at least three and more preferably at least four sites at which hydrogen bonds may be formed are present. These substituents are preferably situated symmetrically at different positions on the macrocyclic compounds. The preferred substituents which may be introduced into the macrocyclic compounds in order to form the derivatives useful according to this invention are those which contain at least one hydroxyl, carboxylate, primary amine or secondary amine function.

A preferred group of macrocyclic compounds from which derivatives useful according to this invention may be prepared are the tetrapyrrolic macrocycles especially the porphyrins and the phthalocyanines.

Especially valuable for use are the porphyrins of the Formula I



wherein R_1 , R_2 , R_3 and R_4 which may be the same or different represent a monovalent group comprising a heterocyclic ring comprising at least one nitrogen atom. The preferred compounds are those wherein the substituents R are identical and represent an imidazole pyrimidine or purine group. The most preferred compounds are those in which a nitrogen atom within the heterocyclic ring of the substituent is at the β position relative to the macrocyclic ring. The most preferred compounds are those wherein the substituents R represent imidazole groups and the most preferred compound is mesotetrakis(2-imidazolyl) porphyrin.

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The porphyrins having the Formula I may be prepared by syntheses known in the art. In particular, by the Rothmund synthesis in which pyrrole is added to a solution of an aldehyde having the formula $RCHO$ wherein R represents any of the substituent groups R_1, R_2, R_3, R_4 as defined above in propionic acid.

The 1:1 metal complexes of the tetrapyrrolic macrocyclic compounds described above may also exhibit conduction properties and molecular-electronic devices comprising such complexes form a further aspect of this invention. These complexes may be prepared using processes known to be useful in the art. The nickel, palladium and platinum complexes of the porphyrins and phthalocyanines are especially useful and form a preferred aspect of this invention. The ferric iron and cupric copper complexes are also of particular value. The metal complexes may find particular application as a conducting material in molecular-electronic devices since they may exhibit both proton and electronic conduction. Devices wherein the conducting material exhibits this dual conduction capability form another aspect of this invention.

The invention is illustrated by the following examples.

Example 1

Mesotetrakis(2-imidazolyl)porphyrin (TIP), was prepared via the Rothmund procedure by refluxing equimolar amounts of imidazole-2-carboxaldehyde and pyrrole in propionic acid. Analytically pure product was obtained by washing the solid precipitated from the cooled reaction mixture with chloroform, acetone and methanol.

The material could not be chromatographed on silica gel. The product was found not to be soluble in neutral aqueous solutions. However, it was soluble in solutions at $pH = 2$ or less.

Uv/visible spectra recorded between 400 nm and 700 nm and from $pH = 2$ (0.01M HCl, porphyrin free-base) to $pH = -1.08$ (12M HCl, porphyrin dication) did not show a coherent set of pH -

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dependant isobestic points for both the B band and Q band spectra.

The IR spectrum of the product (KBr disc) shows a broad, intense absorption between 2400 cm^{-1} and 3600 cm^{-1} , similar to that shown by imidazole.

Samples of TIP were therefore subjected to proton-conductivity studies, along with tetraphenyl porphyrin (TPP) which was used as a non-hydrogen bonded reference compound.

Compressed discs of TIP and TPP were prepared. These were retained between spring-loaded electrodes composed of Pt black electrochemically deposited on a copper substrate in a vacuum-tight environment, in which the partial pressure of water was closely controlled.

Initial D. C. conductivity measurement on a TIP sample under nitrogen, without prior evacuation of the test cell to remove water, gave a conductivity of $1.2 \times 10^{-6}\text{ S m}^{-1}$. Under the same conditions, the TPP sample gave a much lower conductivity of $< 3 \times 10^{-14}\text{ S m}^{-1}$. Dehydration of the samples by evacuating the test cell, reduced the conductivity of the TIP to $1.6 \times 10^{-11}\text{ S m}^{-1}$, while that of the TPP remained virtually unchanged at $1 \times 10^{-14}\text{ S m}^{-1}$.

Another sample of TIP was evacuated overnight at 10^{-2} torr, to remove bound water. It was then allowed to equilibrate in the test cell with an atmosphere containing water vapour at 11.3% partial pressure. The conductivity of the TIP sample was then measured and found to be $6.8 \times 10^{-12}\text{ S m}^{-1}$. A pulse of dry hydrogen gas was then admitted to the cell and the conductivity was observed to rise by nearly four orders of magnitude to $2.8 \times 10^{-8}\text{ S m}^{-1}$, demonstrating that conductivity in TIP is protonic and hydration dependant.

Evidence that TIP has a stacked arrangement of monomeric subunits in the solid state has, however, been provided by powder X-ray diffraction studies. While the data obtained could not be unequivocally indexed, solutions obtained by a program were consistent with there being one short crystallographic

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axis. Values for the unit cell dimensions obtained in this way are:-

$$a = 3.6 \pm 0.2 \text{ \AA}; \quad b = 17.0 \pm 0.3 \text{ \AA}; \quad c = 20.65 \pm 0.25 \text{ \AA}$$

Example 2

5 The porphyrin mesotetrakis (2-imidazolyl) porphyrin (TIP)
(10mgs; 0.0175mM) was warmed with stirring in dilute
hydrochloric acid (0.01M; 3ml) until it dissolved. UV/visible
spectroscopy of this solution showed a four banded visible
spectrum demonstrating that the TIP is not protonated on its
10 central nitrogen atoms.

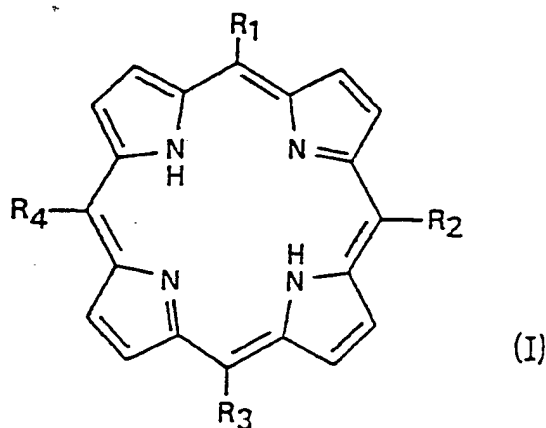
A saturated aqueous solution of nickel chloride (10mls) was
then added with warming. The UV/visible spectrum showed a
collapse of the four banded spectrum to a two banded spectrum
after a period of about three hours.

15 The mixture was allowed to cool to ambient temperature then
several drops of 0.880 ammonia were added. The 1:1 nickel
porphyrin complex precipitated out leaving the excess nickel in
solution in the form of its hexamine complex.

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What we claim is:

1. A molecular-electronic device wherein the conducting material comprises a macrocyclic compound which is capable of forming columnar stacks said compound containing at least one substituent capable of forming a hydrogen bond as part of its molecular structure.
2. A device according to claim 1 characterised in that hydrogen bonds are formed between adjacent macrocyclic compounds in a columnar stack.
3. A device according to claim 2 characterised in that at least three hydrogen bonds are formed between the adjacent macrocyclic compounds.
4. A device according to claim 3 characterised in that at least four hydrogen bonds are formed between the adjacent macrocyclic compounds.
5. A device according to any of the preceding claims characterised in that the macrocyclic compound is a tetrapyrrolic macrocyclic compound.
6. A device according to claim 5 characterised in that the tetrapyrrolic macrocyclic compound is a phthalocyanine.
7. A device according to claim 5 characterised in that the tetrapyrrolic macrocyclic compound is a porphyrin.
8. A device according to claim 7 characterised in that the porphyrin has the formula:



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wherein at least three of the substituents R_1 , R_2 , R_3 and R_4 which may be the same or different represents a group comprising at least one hydroxyl, carboxyl primary amine or secondary amine function.

- 5 9. A device according to claim 8 characterised in that the substituents R_1 , R_2 , R_3 and R_4 represent a heterocyclic group comprising at least one nitrogen atom as part of the cyclic species.
- 10 10. A device according to claim 9 characterised in that the substituents are selected from the group comprising imidazole, pyrimidine and purine.
11. A device according to claim 10 characterised in that the substituent is a 2-imidazole group.
12. A device according to claim 11 characterised in that the
15 macrocyclic compound is mesotetrakis(2-imidazolyl) porphyrin.
13. A device according to any of the preceding claims characterised in that the mode of conduction is at least partially that of proton conductance.
14. A device according to any of the preceding claims
20 characterised in that the macrocyclic compound is present as a 1:1 metal complex.
15. A device according to claim 14 characterised in that the metal complex is a nickel, palladium, platinum, ferric iron or cupric copper complex.
- 25 16. A device according to either of claims 10 or 11 characterised in that the macrocyclic compound is present in the form of its nickel complex.
17. A macrocyclic compound which is useful as a conducting material in a device according to any of claims 1 to 13.
- 30 18. Mesotetrakis(2-imidazolyl) porphyrin which is characterised in that it exhibits proton conductance in the solid state.
19. A process for the preparation of a macrocyclic compound useful in a device according to claim 8 which comprises reacting pyrrole with an aldehyde having the formula $RCHO$ wherein R
35 represents any or all of the substituents R_1 , R_2 , R_3 and R_4 .

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20. A device according to any of the preceding claims substantially as hereinbefore described with reference to the foregoing examples.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/G8 92/00338

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 H01B1/12; C07D487/22

II. FIELDS SEARCHED**Minimum Documentation Searched⁷**

Classification System

Classification Symbols

Int.Cl. 5

H01B ;

C08G ;

C07D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Indicated in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 134 171 (ELF AQUITAINE) 13 March 1985 see the whole document	1,5-8, 13-17
A	US,A,4 563 301 (K.J.WYNNE &AL) 7 January 1986 see claims 1-11	1,5-7, 14-17
A,P	DE,A,4 001 158 (BASF) 18 July 1991 see the whole document	1,5-7, 13-15
A	US,A,4 304 719 (K.J.WYNNE & AL) 8 December 1981 see the whole document	1
A	US,A,2 951 799 (D.B.SHARP) 6 September 1960 see the whole document	18,19

¹⁰ Special categories of cited documents :¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance¹⁰ "E" earlier document but published on or after the international filing date¹⁰ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)¹⁰ "O" document referring to an oral disclosure, use, exhibition or other means¹⁰ "T" document published prior to the international filing date but later than the priority date claimed¹⁰ "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹⁰ "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹⁰ "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹⁰ "A" document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

23 APRIL 1992

Date of Mailing of this International Search Report

13. 05. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

DROUOT M.C.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9200338
SA 56782**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 23/04/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0134171	13-03-85	FR-A- 2550344	08-02-85
		CA-A- 1224843	28-07-87
		DE-A- 3472005	14-07-88
		JP-A- 60058546	04-04-85
		US-A- 4526674	02-07-85
US-A-4563301	07-01-86	None	
DE-A-4001158	18-07-91	None	
US-A-4304719	08-12-81	None	
US-A-2951799		None	

L4 ANSWER 15 OF 21 CAPLUS COPYRIGHT 2000 ACS

AN 1992:624435 CAPLUS

DN 117:224435

TI Molecular-electronic devices containing conductive macrocyclic compounds, the macrocyclic compounds, and their preparation

IN Milgrom, Lionel Robert

PA British Technology Group PLC, UK

SO PCT Int. Appl., 11 pp.

CODEN: PIXXD2

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9215099	A1	19920903	WO 1992-GB338	19920225
	W: JP, US				
	RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE				
	GB 2253209	A1	19920902	GB 1992-4028	19920225
	EP 526609	A1	19930210	EP 1992-905374	19920225
	R: DE, FR, GB, IT, NL, SE				
	JP 06503204	T2	19940407	JP 1992-505053	19920225
PRAI	GB 1991-3991		19910226		
	WO 1992-GB338		19920225		

OS MARPAT 117:224435

AB Derivs. of macrocyclic compds. capable of forming columnar stacks in the solid phase (e.g., porphyrin and phthalocyanines) and which can form H bonds show enhanced elec. conduction. A preferred compd. is mesotetrakis(2-imidazolyl)porphyrin. The derivs. may exhibit proton conduction, and the 1:1 metal complexes are valuable insofar as they may exhibit both proton and electron conduction.

IT 110766-04-6

RL: PRP (Properties)

(elec. conductive, mol.-electronic devices contg.)

RN 110766-04-6 CAPLUS

CN 21H,23H-Porphine, 5,10,15,20-tetra-1H-imidazol-2-yl- (9CI) (CA INDEX NAME)

